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A Mechanical, High Surface Area and Solvent-Free 'Powder-to-Electrode' Fabrication Method for Screening OER Catalysts

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Keywords: OER, powder, electrocatalysts, PTFE, pressed-disc.

Abstract

The screening of new OER materials routinely involves fabricating electrodes from powders using methods which are often time consuming and may involve using solvents and/or conductive materials that can alter the OER activity of the powder. Herein, a new mechanical, solvent-free method for fabricating electrodes for OER is described in which an electroactive material under test, mixed with a small amount of PTFE powder (ca. 10 wt%), is pressed onto Pt powder to create a permanent, robust electrode that can be used in a rotating disc electrode set-up. This new method of fabricating electrodes is compared to the well-known dropcast on Glassy Carbon (GC) method, using commercially available materials: RuO₂, Co₃O₄ and NiO. The results show that the mechanical route produces much better OER performances, in terms of overpotential and stability, for the commercial metal oxide on the pressed discs when compared to the dropcast GC method. Finally, it is shown that this mechanical, high surface area, solvent-free electrode fabrication technique can also be achieved using silver, rather than platinum, as the conducting, support material.

1. Introduction

In recent years the optimisation of OER materials has been a particular focus of research among the scientific community as part of a sustained effort to build an efficient, low cost, stable solar-driven water splitting system.[1-9] The best known OER catalysts are the platinum group metal (PGM) oxides, RuO₂ and IrO₂ which exhibit overpotentials at 10 mA cm⁻² [5, 10] however, these materials are rare and expensive. As a consequence, the majority of the OER work focuses on the identification of materials that exhibit a low OER overpotential with high stability and are either less expensive earth-abundant materials, or an amalgamation of the latter with a small amount of PGM oxide.[1, 10-14] Obviously, due to the extensive number of possible material candidates for the OER, a rapid screening method is required. Currently, OER studies involve the routine fabrication of electrodes from powders by depositing them onto conducting substrates by various methods, listed in Table 1, and the most popular of which is by drop-casting a dispersion of the metal oxide under investigation onto a glassy carbon, GC, electrode.

Table 1. 'Powder-to-electrode' methods used for OER studies

WOC	η_{10} (V)	Deposition Method/ Substrate	Electrolyte used for OER studies	Solvent /polymer	Annealing Temp/ drying	Ref
Ni(OH) ₂	0.36	spray coating/ Ni foam	1 M NaOH	ethanol /Nafion	dry under N ₂ flow	[15]
Fe ₂ O ₃	0.39					
Co ₃ O ₄	0.5	dropcast/ discs. GC	1 M NaOH	2-propanol /Nafion	60 °C for 10 mins in oven.	[5]
NiO	0.43					
Mn ₂ O ₃	0.53					
IrO ₂	0.38					
RuO ₂	0.38					
Co ₃ O ₄	0.53	dropcast/ GC discs	0.1 M KOH	ethanol /Nafion	dry in air.	[16]
IrO ₂	0.45	dropcast/ disc GC	0.1 M KOH	ethanol/cond uctive carbon and Nafion	dry in air.	[17]
Co ₃ O ₄	0.47	dropcast/ discs Au	0.1 M KOH	ethanol	dried at 120 °C for 2 hours in vacuum.	[18]

NiFe LDH/ CNT*	0.26		1 M KOH	ethanol/ Nafion	dry in air.	[19]
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*LDH/CNT = Layered double hydroxide/carbon nanotube

The electrodes produced using these methods are usually not robust physically and result in poor electrochemical stability. In literature, this can be observed from the various stability studies (chronopotentiometry or multi-cycling) when a decrease in activity is observed over time, which is probably due to properties associated with the support material and/or the degrading of the active material therefore alternative support materials are sought after.[20, 21] In addition, the usual casting/coating methods often use solvents, such as EtOH and 2-propanol, table 1, and require the addition of materials, such as CNTs and Nafion, to improve the conductivity of the film, which can influence the performance of the materials.[22-24] Another disadvantage associated with the usual ‘powder to electrode’ methods is the risk of contamination when using the same substrate to test various powder electrocatalyst candidates. Finally, in most cases, the underlying substrate, is often costly and needs to be re-used, thus rendering it infeasible to keep any prepared drop-cast electrode for any length of time.

In this paper we propose a simple, mechanical approach to fabricate electrodes from powders to test as OER catalysts, in which the electroactive material under test is mixed with PTFE powder and pressed into a thin layer on an underlying bed of Pt powder to yield a disc, which can then be used as an RDE. Herein, the electrochemical characteristics of a number of different metal oxide electrodes made using this method are compared with those made using the common drop-cast method and the results are reported below.

2. Experimental Details

2.1 Materials

The ruthenium (IV) oxide (99.9%), nickel (II) oxide (< 50 nm particle size, 99.8%), cobalt (II.III) oxide (< 50 nm particle size, 99.5%), poly(tetrafluoroethylene) (PTFE) powder (1µm particle size) and Nafion 117 solution were all obtained from Sigma Aldrich. The platinum (200 mesh, metals basis, 99.98%) and silver (325 mesh, metals basis, 99.98%) powders were obtained from Alfa Aesar and the NaOH pellets from Scientific and Chemical Supplies Ltd.

2.2 Pressed Disc Fabrication

In this work, a typical pressed disc electrode, containing a potential water oxidation powder catalyst, was prepared as follows: 300 mg of the Pt powder were placed in an IR pellet press die (Specac) with a 4 mm internal diameter. The powder was tamped down by hand using the stainless steel IR die rod. Then, a powder mixture comprising of 0.9 mg of the metal oxide powder catalyst under test, and 0.1 mg of an inert binder, PTFE powder, were added to the die. After gentle tamping, a robust (catalyst/PTFE)/Pt composite disc was then fabricated by applying 2 T of pressure for 10 s to the (metal oxide/PTFE)/Pt using a hydraulic IR press; a schematic illustration of this process is illustrated in Fig. 1 (a). Pt powder was chosen as the backing material for our catalysts as it is: (i) easily pressed to obtain a physically robust underlying support conductor, (ii) commonly used as a substrate for OER and (iii) known to be an unexceptional as an OER catalyst, but stable as an electrode material for such work.[25-27]

Photographs of a typical pressed disc, with commercial RuO₂ as the black, electro-active top layer are illustrated in Fig 1. (b) and (c). The SEM and EDX analysis of this disc are illustrated in Fig 1. (d) - (f). The EDX analysis shows that there is only a small amount of Pt on the surface of the electrode, Fig. 1(f), and mainly at the edge. In contrast, most of the surface of the electrode is made up of the pressed metal oxide powder (Ru La1, Fig. 1(e)). The pressed disc is then inserted into a RDE set-up (ALS co. Ltd, 012623), so as to allow its assessment as an electrocatalyst.

2.3 Dropcast electrode fabrication

The metal oxide ink dispersions used to dropcast onto the GC discs were prepared using an established procedure.⁶ Briefly, this involved placing 100 mg of the relevant powder, 4 ml of deionised water, 1 ml of ethanol and 50 µl of Nafion into a vial. The metal oxide ink dispersion was sonicated for 10 mins and then 45 µl of the ink were dropcast onto a GC disc. The ink was dropcast every 5 mins onto the RDE disc until all 45 µl of the ink were deposited onto the disc. The disc was allowed to dry in the oven at 60 °C between each deposition and then allowed to dry for 30 mins in the oven.

2.4 Other methods

Scanning Electron Microscopy (SEM) measurements were carried out using a FEI Quanta™ 250 SEM with a spot size of 4 mm, working distance of 10 mm and an accelerating voltage of 20 kV. Elemental mapping was carried out using the same instrument coupled to an EDX detector from Oxford Instruments.

2.5 Electrochemical methods

All electrochemical measurements were conducted using a three electrode cell. The working electrode consisted of a pressed Pt or Ag disc with the active material, prepared as described in Section 2.1, or a drop-cast-coated commercial GC disc (ALS co. Ltd, 013338). In both cases, the disc electrodes were inserted into the RDE disc assembly (ALS co. Ltd) then screwed into the rotating disc set-up. All working electrodes had a diameter of 4 mm and had a mass loading of ca. 0.9 mg.

For all the OER measurements, the counter and reference electrodes were a graphite rod and Hg/HgO electrode, respectively, the electrolyte was 1 M NaOH and the working electrode was spun at 1500 rpm. Linear Sweep Voltammetry (LSV) studies were conducted at a scan rate of 0.1 mV/sec. Chronopotentiometric stability tests were run by applying a constant current density of 10 mA cm⁻². The solution resistance values, used to iR correct the LSV, were determined by Electrochemical Impedance Spectroscopy (EIS). The EIS measurements were conducted in the frequency range of 10000 Hz to 0.1 Hz in a non-Faradaic region. In this study, typical resistance values for all metal oxide electrodes were between 7-11 Ω . Electrochemical surface area (ECSA) experiments were carried out by performing multiple CV experiments in a non-Faradaic region (typically in the 0 - 0.3 V vs. Hg/HgO region) at various scan rates (typically 1 – 200 mV s⁻¹).

3. Results and Discussion

3.1 Pressed RDE vs. Dropcast RDE for OER using a variety of different metal oxides

The LSV curves for the metal oxide, RuO₂, CO₃O₄ and NiO, electrodes prepared by the pressed Pt disc method and dropcast onto GC method are illustrated in Figs. 2(a-b). LSV analysis yielded overpotential values, η_{10} , at a current density of 10 mA cm⁻², which are summarised in Table 2, along with the ECSA data. In all cases the overpotential values for the pressed electrodes were found to be much lower than those found for the drop-cast GC electrodes, the main cause for which appears to be the much greater ECSA values of the pressed discs, compared to the GC electrodes, see table 2. Note that the η_{10} data reported here, using the dropcast/GC technique, compares well with those reported by others⁶, using the same technique and metal oxides (see the literature values in parentheses in table 2). The superior activity observed for the Pt pressed discs is clearly not a synergistic enhancement between the underlying Pt metal and the active material. This can be observed from the LSV curves of the RuO₂ on a pressed Pt disc and dropcast on a commercial Pt disc, Figure 2(a), as the RuO₂/Pt commercial disc is shifted to more anodic potentials compared to the RuO₂/Pt pressed disc. One should note that the enhancement in the NiO on the pressed Pt over dropcast on the GC can also be explained by the large increase in the ECSA of the NiO on the Pt

pressed disc. From table 2, the ECSA of the NiO on the pressed Pt is 400 cm² while the same material on the GC disc is 1.6 cm². Additionally, the reusability of the electrodes are illustrated in Fig 2(a), as the activity of a RuO₂/Pt pressed disc shows only a small decrease (~40 mV at 10 mA cm⁻²) when kept in storage in air for four months.

Unlike the drop-cast GC method, the pressed disc method also created electrodes of great stability, as demonstrated by running chronopotentiograms at 10 mA cm⁻², Figs. 2 (c-d). The results of this work demonstrate that, as noted by others [5, 20, 21, 28], metal oxides drop-cast onto GC electrodes are not very robust physically, so that with prolonged oxygen evolution the metal oxide becomes less active. This effect is strikingly illustrated by the sharp upward turn in the chronopotentiograms observed for all the drop-cast GC electrodes tested, see Fig. 2(d), and particularly so for the GC NiO electrode, with no coating lasted > 2.5 h. This sudden loss in activity observed for the metal oxides on the GC may be due to the passivation of the GC support, recently reported by Geiger *et al.*, which makes our Pt pressed discs an even more attractive option.[20] In contrast, the pressed Pt discs showed no evidence of wear, even after 20 h of use, under identical experimental conditions, Fig. 2(c). Additionally, if required, the Pt metal can be easily recovered and re-used by cutting or polishing off the top 'electrocatalyst' layer. However, these electrodes are not that expensive, according to Johnson Matthey the current cost of Pt is \$33 per gram therefore a pressed Pt disc electrode would cost approximately \$10 each, if using 300 mg of Pt for the underlying support.[29] Also, the objective for fabricating these pressed discs is that they can be initially used for a prolonged period due to their excellent stability, Fig. 2(c), then reused and retested to monitor the change in activity at a later date, Fig 2(a).

Table 2. Summary of OER results

	Commercial powders on pressed Pt disc.		Commercial powders on commercial GC disc.	
	η (V) at 10 mA cm ⁻²	ECSA (cm ²)	η (V) at 10 mA cm ⁻²	ECSA (cm ²)
RuO₂	0.25	124	0.34 (0.38)*	5
Co₃O₄	0.32	154	0.36 (0.5)*	28
NiO	0.30	400	0.8 (0.43)*	1.6

*Value in brackets are reported by others for the same commercial metal oxides on a GC disc.[5]

3.2 Pressed RDE electrode fabrication: Using silver powder

In order to demonstrate that the pressed electrodes can be fabricated using a less expensive underlying conducting substrate, the commercial RuO₂ powder used earlier was again pressed into a

RDE disc but this time using Ag powder as the conducting metal support, instead of Pt. The LSV curve and stability test for the RuO₂ pressed on the Ag powder disc electrode, Fig. 2(e)-(f), were almost identical to those for the RuO₂/Pt pressed electrodes. From the LSV curves of the RuO₂/Ag pressed electrode the overpotential was determined to be 0.26 V at a current density of 10 mA cm⁻². The LSV of the bare Ag disc is relatively flat, apart from the Ag to AgO peak at about 0.3 V vs OER overpotential, Fig. 2(e). The Ag/AgO oxidation peak doesn't influence the OER performance of the RuO₂ as it is only a redox peak, much like that observed for the Ni(II)/Ni(III) redox peak when Ni metal foam supports are used for the OER. [15] Thus, using Ag as the backing material, instead of Pt, reduces the fabrication cost of the pressed discs. These findings are interesting as Ag substrates are used throughout the literature for numerous electrochemical applications including OER, biomolecule immobilisation and glucose sensing.[25, 30, 31]

4. Conclusions

A mechanical, solvent-free route to produce electrodes for the OER is presented. The results show that the pressed Pt disc method produces electrodes that exhibit superior OER performances in comparison to the usual dropcast method, on GC, for the same powder test metal oxide materials. This enhancement is most probably related to the increased electrochemical surface areas of the pressed disc electrodes over the dropcast GC ones. Other work shows that the cost of preparing the mechanical electrodes can be reduced markedly by using Ag as the underlying support material. This mechanical, solvent-free route for producing OER electrodes offers a new, simple route to electrode fabrication which will help in screening any new potential electrode materials for use in the OER and other reactions. In addition to being simple and fast and producing electrodes with high electrochemical surface areas, it also creates electrode discs which can be used again, unlike the more commonly employed drop-casting GC method.

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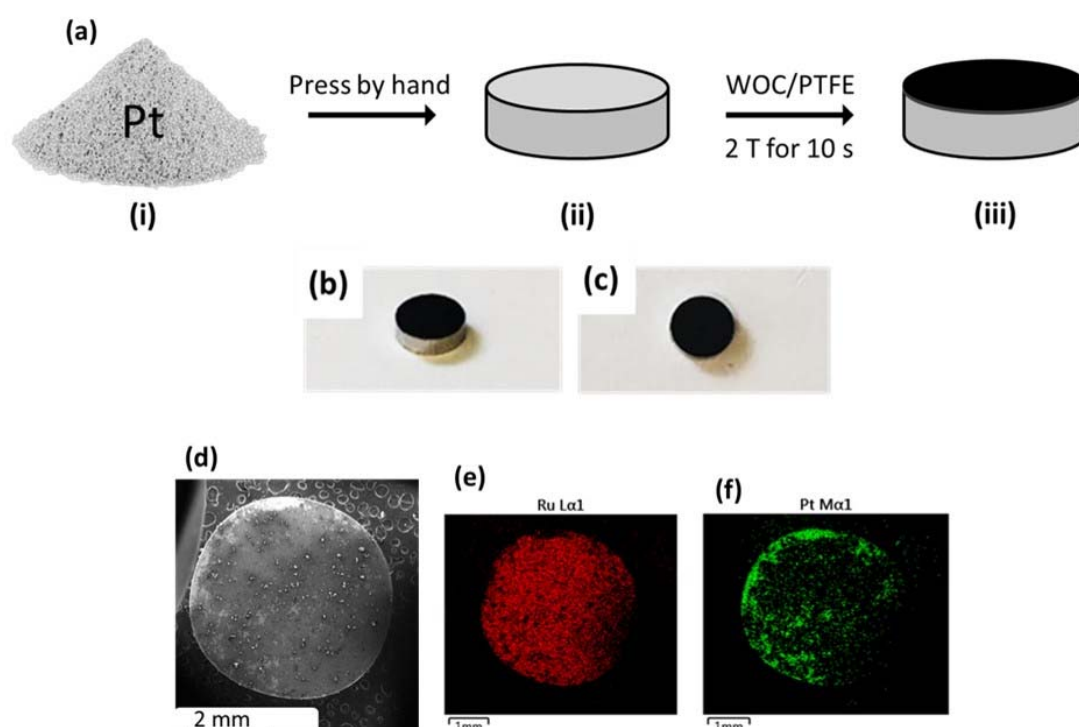


Fig. 1 (a) Schematic of the pressed disc fabrication process with (b) side and (c) top images of a typical pressed RuO₂/Pt disc (d) SEM image of a pressed RuO₂/Pt disc (e) Ru Lα1 and (f) Pt Mα1 EDX map of a pressed RuO₂/Pt disc.

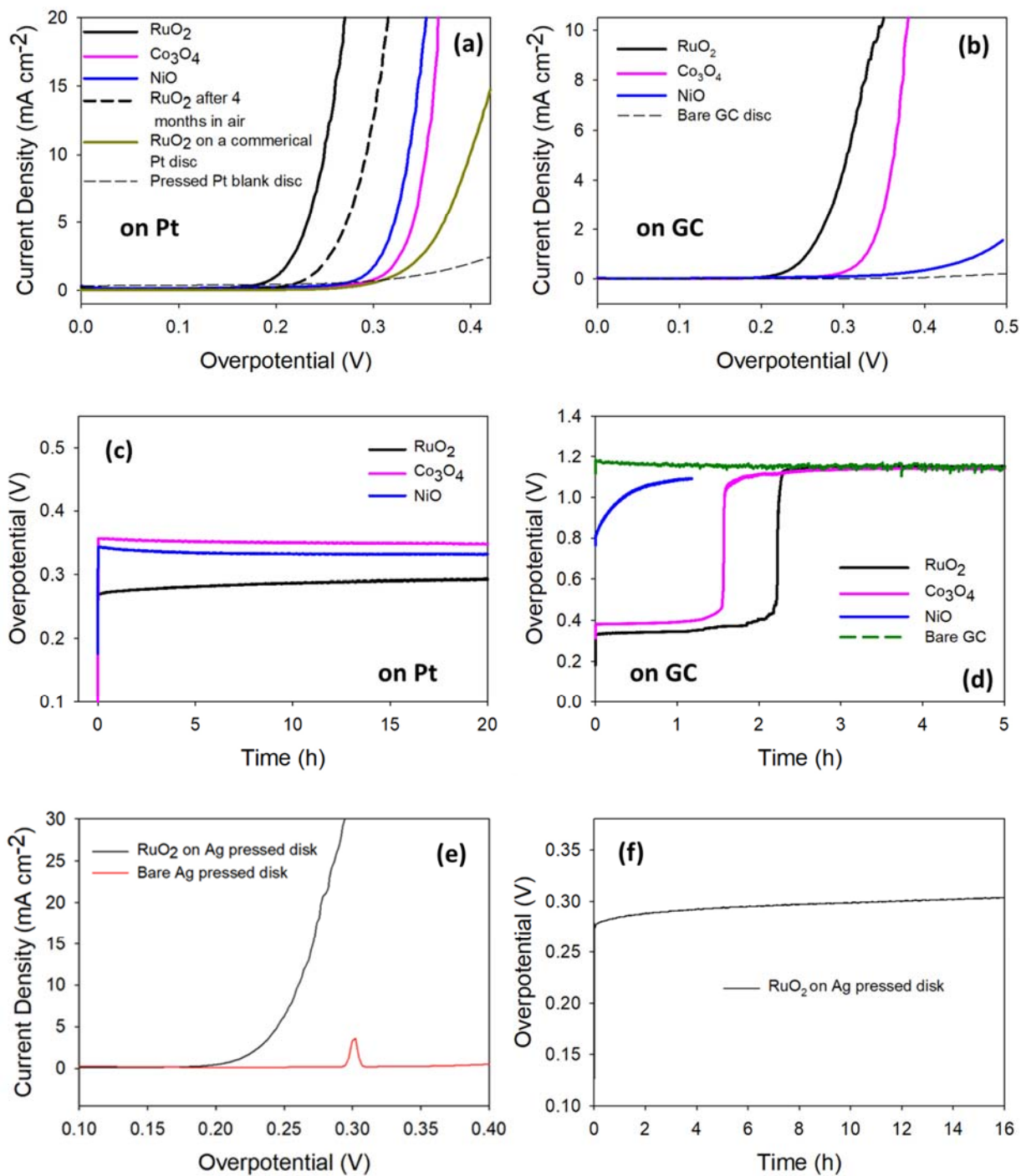


Fig. 2. LSV curves of the commercial RuO_2 , Co_3O_4 and NiO on (a) pressed Pt discs with RuO_2/Pt after 4 months in air and RuO_2 on a commercial Pt disc (b) GC discs. Stability tests for the commercial RuO_2 , Co_3O_4 and NiO on (c) pressed Pt discs (d) GC discs. (e) LSV curve of the commercial RuO_2 on a pressed Ag disc and (f) Stability test of the commercial RuO_2 on a pressed Ag disc.